Enclosure 10

PATENT SPECIFICATION

984,633

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COMPLETE SPECIFICATION

NO DRAWINGS

Manufacture of Epoxy Resins

We, SOCIETE D'ELECTRO - CHIMIE, D'ELECTRO-METALLURGIE ET DES ACIERIES ELECTRIQUES D'UGINE, a French Body Corporate of 10 rue du General Foy, Paris VIIIe, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the manufacture of epoxy resins, in particular of epoxy resins having improved resistance to combustion. The term "epoxy resins" as used in this Specification and appended Claims is deemed to mean compounds containing more than one epoxy group per molecule.

Epoxy resins such as those marketed under the Trade Marks "Ardalite" or "Epon" are well known products. They are generally obtained by the action of epichlorhydrin on a phenol having at least two hydroxyl groups. These resins can be transformed into thermo-hardened products by hardening agents having either an acidic (e.g. maleic anhydride) or amine (e.g. triethanolamine) character. All these resins, however, burn in air, and this characteristic of combustibility considerably limits their field of application.

It has been attempted to meet this difficulty by adding mineral fillers for example talc, kaolin, to the resin. The combustibility of the resins has, however, been little reduced thereby, and to the detriment of their physical and mechanical characteristics.

It is well known that the introduction of chlorine into a molecule confers on the product obtained a resistance to combustion which is proportional to the amount of chlorine introduced. It was a natural consequence of this to attempt to introduce chlorine, in different forms, into epoxy resins. Various processes have been proposed to this end.

Thus British Patent No. 741,870 filed November 10th, 1952, mentions polyepoxides of chlorinated polyethers containing in their molecule only aliphatic chlorine which renders the resin unstable to heat. Moreover the proportion of chlorine in the final product does not exceed 10 to 11%, which is insufficient to ensure satisfactory incombustibility.

In French Specification No. 1,154,500, filed June 4th, 1956, the resin is chlorinated by adding pentachlorphenol or its glycidyl ether, But the extent of addition cannot then exceed 65% without risk of exudation, and even then, the maximum proportion of chlorine in the resin is only 43.5%, and a considerable part of the pentachlorophenol is not chemically bound. In order to obtain a product in which the pentachlorophenol is chemically bound, bisphenol A and pentachlorophenol are condensed with epichlorhydrin, but under these conditions a chlorine proportion of 15% is the maximum obtainable in practice. Although in an example in the said Specification a proportion of 30% is mentioned, such a proportion corresponds to a monofunctional resin which is not further polymerisable.

British Specification No. 744,388, discloses the introduction of chlorine by means of the hardening agent, which is chlorinated ethylenic diacid, in particular tetrahydrophthalic hexachloroendomethylene anhydride. But since the dissolution of this hardening agent in the resin is slow, it is necessary, in order to obtain a homogeneous mixture, to operate at a relatively high temperature. The hardening then occurs very quickly, even during the dissolution, which renders difficult the utilisation of the

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product and is very prejudical to its commercial development.

In British Specification No. 773,655 this difficulty is eliminated by introducing the hardening agent in solution in pentachlorodiphenyl, but the corresponding resins can be hardened only when hot, their hardening time is long, and they contain only 30% of chlorine, a part of which is in fact not chemically bound.

In French Specification 6o. 1,180,194 it is proposed to utilize as a starting product the chlorinated derivatives of bisphenol A, more precisely the nuclear chlorinated derivatives of bis p-hydroxyphenyl-2,2-propane. These products are obtained by direct chlorination of bisphenol A, but the yields are mediocre: 40 to 45% in the case of derivatives with four atoms of chlorine per molecule. This Specification also describes higher proportions of chlorine, but in practice it is not possible to go beyond four atoms of chlorine without coming up against great difficulties of purification. The epoxy resins comprising tetrachlorobisphenol A contain 27 to 30% chlorine.

It is a main object of the present invention to provide a process for obtaining from chlorodiphenols rich in chlorine and easily accessible economically and technically, epoxy resins characterised by a high proportion of chemically bound chlorine, good self-extinguishing properties measured according to A.S.T.M. D 757-49, high Rockwell hardness, and high Vicat softening point. The remaining properties of these resins are not impaired.

According to the present invention there is provided a process for the manufacture of epoxy resins having improved resistance to combustion, which comprises reacting a chlorhydrin with at least one isomer of octochlorodihydroxydiphenyl in an alkaline medium.

The alkaline agent is advantageously sodium hydroxide, preferably in aqueous solution, but the other alkaline bases are also suitable. The chlorhydrin generally used is epichlorhydrin, but the reaction is applicable to other chlorhydrins, for instance glycerol dichlorhydrin. Preferably the chlorine content is at least 50% by weight of the resin.

Octochlorodihydroxydiphenyls may be prepared by the following method.

In French Specification No. 1,229,815 there is described a process for obtaining good quality decachlorodiphenyl cheaply and simply. Phenolisation of this product by sodium hydroxide yields octochlorodihydroxy diphenyl isomers, which constitute, according to the present invention, a starting chlorinated diphenol for the new epoxy resins. An octochlorodihydroxydiphenyl isomer may be used either alone or together with other compounds which do not react therewith but which react with a chlorhydrin to form an epoxy resin, such as bisphenols and in particular bisphenol A.

By varying the proportion and the concentration of the alkaline agent, and/or the nature and the excess of the chlorhydrin, a series of resins, ranging from solid products to syrups may be obtained according to the degree of epoxy equivalent.

All these resins can be hardened either in the cold or when hot in the presence of known hardening agents, such as polyacids and polyamides. They have, after hardening, perfect self-extinguishing properties and fulfil the A.S.T.M. D 757-49 test: when placed in the flame of a blowpipe they char, but they extinguish instantaneously upon removal from the flame.

Of the following Examples, which are given by way of illustration only, in order that the invention may be more clearly understood, Nos. 1 to 5 show various methods for carrying out the process according to the invention, while Nos. 6 to 8 show methods for hardening these resins.

EXAMPLE 1.

To a stirred solution of 231 parts by weight of a mixture of isomers of octochlorodihydroxydiphenyl which were not separately identified in 321 parts by weight of 10% sodium hydroxide 57.8 parts by weight of epichlorhydrin were progressively added. The mixture was brought to 100°C. in 1 hour 30 minutes and maintained at this temperature for one hour.

A white solid was thus precipitated, which was crushed and washed with boiling water until no further chlorine ions could be detected in the wash-water. After drying a solid of chlorine content 53.5% was obtained, having a softening point between 150 and 165°C., and an epoxy equivalent of 1,040.

EXAMPLE 2.

The same method as in Example 1 was employed, but with the 231 parts by weight of diphenol were reacted 115.6 parts by weight of epichlorhydrin and 575 parts by weight of 10% sodium hydroxide.

Thus were obtained 242 parts of a white powder having a chlorine content of 54.5% and an appearance similar to that of Example 1, but whose softening point was 175-205°C. and epoxy equivalent 1,670.

EXAMPLE 3.

Into an agitated suspension of 231 parts by weight of the diphenol in 115.6 parts by weight of epichlorhydrin and 125 parts by weight of water, 400 parts by weight of 10% sodium hydroxide were introduced over a two-hour period while maintaining the temperature at 40°C. The mixture was stirred for 6 hours at 40°C.

The resin was extracted with chloroform

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and the organic solution was washed twice in water, then in water made acid with HCl, again with water, then finally dried. The chloroform was distilled off and the resin dried in a drying chamber at 150°C.

242 parts of an amber-coloured resin having a chlorine content of 53% and a softening point of 60-85°C., of epoxy equivalent 900, were obtained.

EXAMPLE 4.

462 parts by weight of the diphenol were dissolved in 925 parts by weight of epichlorhydrin; the solution was heated to 108°C. and 164 parts by weight of 48.9% aqueous solution of sodium hydroxide were progressively added. The sodium hydroxide addition was made in one hour at a temperature between 105 and 108°C. The water formed an azeotropic mixture with the epichlorhydrin and was thus removed from the reaction mixture. The excess epichlorhydrin was distilled off in a water-bath under reduced pressure. 613 parts by weight of epichlorhydrin were recovered.

Monochlorobenzene was added to the content of the balloon-flask, and the suspension obtained was then filtered to separate the precipitated sodium chloride. The monochlorobenzene was distilled off in a water-bath under reduced pressure, of 1 mm. of Hg.

620 parts by weight of a yellow syrup of epoxy equivalent 428 and chlorine content 51.5% were obtained.

EXAMPLE 5.

The same process as in Example 4 was employed, but with an equimolecular mixture of the diphenol and bisphenol A, i.e. 115.5 parts by weight of the diphenol and 57 parts by weight of bisphenol A, which were dissolved in 462.5 parts by weight of epichlorhydrin. In one hour, at 105-108°C., 81.8 parts by weight of 48.9% sodium hydroxide were added.

313 parts by weight of epichlorhydrin were recovered.

216 parts by weight of a soft resin, similar to that of Example 4, of epoxy equivalent 331 and chlorine content 50.3%, were thus obtained.

EXAMPLE 6.

5 parts by weight of the resin of Example 1 were dissolved in 8 parts by weight of methyl ethyl ketone and two parts by weight of maleic anhydride were added to the solution. A glass plate was coated with this solution, dried for one hour in the open air, and heated for 16 hours at 150°C.

A transparent, colourless varnish was thus obtained, which could be scratched only with difficulty and had a very good adhesiveness.

EXAMPLE 7.

4.9 parts by weight of maleic anhydride were dissolved when hot in 22 parts by weight of the resin of Example 4. After addition of 0.5 parts by weight of tri-n-butylamine, the homogeneous mixture was poured into a mould coated with polyvinyl alcohol. It was then heated for 14 hours at 130°C. (the mixture gelled in 20 minutes).

A pale yellow, transparent, very hard resin was thus obtained, having a Rockwell hardness of 111.3 and a Vicat softening point of 140.5.

EXAMPLE 8.

25 parts of the resin of Example 4 were dissolved in 25 parts by weight of a mixture of isomers of pentachlorodiphenyl which were not separately identified, and 2.5 parts of N,N'-diethylamino-3-propylamine were added to the solution obtained.

The mixture gelled after 4 hours at the ambient temperature. After 16 hours, it was completely hardened.

In order to improve the indeformability when hot, the hardening could be completed by a heating of 4 hours at 80°C., after which the resin had a Rockwell hardness of 101.3 and a Vicat softening point of 127.

The hardened resins cited in Examples 6, 7 and 8, tested according to A.S.T.M. D 757149, char in the flame of a blow-pipe, but do not continue to burn when they are withdrawn therefrom: they are self-extinguishing.

WHAT WE CLAIM IS:—

1. A process for the manufacture of epoxy resins having improved resistance to combustion, which comprises reacting a chlorhydrin with at least one isomer of octochlorodihydroxydiphenyl in an alkaline medium.

2. A process according to Claim 1 wherein the alkaline medium comprises sodium hydroxide.

3. A process according to Claim 1 or Claim 2 wherein the alkaline medium is an aqueous alkaline medium.

4. A process according to any preceding Claim wherein the chlorhydrin is epichlorhydrin.

5. A process according to any of Claims 1 to 3 wherein the chlorhydrin is glycerol dichlorhydrin.

6. A process according to any preceding Claim wherein at least one isomer of octochlorodihydroxydiphenyl is reacted with the chlorhydrin together with one or more other substances which do not react with the octochlorodihydroxydiphenyl but which do react with chlorhydrin to form an epoxy resin.

7. A process according to Claim 6 wherein at least one isomer of octochlorodihydroxydiphenyl and a bisphenol are reacted with the chlorhydrin.

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8. A process according to Claim 6 wherein the bisphenol is bisphenol A.

9. A process for the manufacture of epoxy resins, comprising reacting a chlorhydrin with at least one isomer of octochlorodihydroxydiphenyl in an alkaline medium substantially as herein described.

10. A process for the manufacture of epoxy resins, comprising reacting a chlorhydrin with at least one isomer of octochlorodihydroxydiphenyl in an alkaline medium substantially as herein described with reference to any of Examples 1 to 5.

11. An epoxy resin manufactured by the process claimed in any preceding Claim.

12. A process of hardening an epoxy resin as claimed in Claim 11 substantially as herein described with reference to any of Examples 6 to 8.

13. Self-extinguishing resins obtained by reacting a chlorhydrin and at least one isomer of octochlorodihydroxydiphenyl, said resins having a chlorine content of at least 50% by weight.

14. Self-extinguishing resins obtained by reacting a chlorhydrin, at least one isomer of octochlorodihydroxydiphenyl and bisphenol A, said resins having a chlorine content of at least 50% by weight.

15. Self-extinguishing resins according to Claim 13 or Claim 14 wherein the chlorhydrin is epichlorhydrin.

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